Paper to be presented at the 12th USAEC Air Cleaning Conference, Oak Ridge, Tennessee, August 28-30, 1972. To be published in the Proceedings.

DRAFT

Conf- 720823--11

**Determination of the Radioactive Nuclides Present in the
Off-Gas Stream Generated by the Head-End Steps in
Reprocessing HTGR Type Fuels***

R. S. Lowrie
C. L. Fitzgerald
V. L. A. Laughen**

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

**On assignment to Institut für Chemische Technologie, Jülich, Germany.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Rey

DRAFT

ABSTRACT

Results of studies to determine the behavior of radioactive nuclides in the gaseous waste streams generated during the reprocessing of spent High Temperature Gas-Cooled Reactor (HTGR) fuel are presented. The fuel is in the form of coated particles of uranium and thorium, bonded into fuel sticks, and inserted into holes in large hexagonal graphite blocks. Spent fuel is reprocessed to recover the bred ^{233}U and the unburned ^{235}U .

Studies were performed on a small scale in a hot-cell using a generalized head-end reprocessing flowsheet. The fuel specimens were crushed, burned to remove as much graphite as possible, and the burner residue separated into appropriate size fractions. Those fractions containing TRISO-coated particles were then ground to break the SiC coating and burned a second time. Residues from each fraction were leached with acid Thorex reagent. The off-gas from each step was collected and analyzed.

Preliminary tests, primarily to measure ^{85}Kr and tritium release, were made using Dragon fuel compacts containing either BISO-coated $(\text{U-Th})\text{O}_2$ sol-gel particles or both TRISO-coated ThC_2 and TRISO-coated UC_2 particles. Burning the BISO-coated $(\text{U-Th})\text{O}_2$ particles released the bulk of the ^{85}Kr (97-98%) and the tritium (98-99%); the remainder was released during the leaching step. The initial burning of the mixed TRISO-coated ThC_2 and TRISO-coated UC_2 fuel released ~7.4% of the ^{85}Kr . Subsequent grind-burn steps released an additional 7.4% of the ^{85}Kr from the ThC_2 particles and 84.5% from the UC_2 particles.

Experiments with the Recycle Test Element (RTE) fuel specimens are designed to permit sampling the off-gas stream for both volatile and entrained fission products. Tests have been completed on a fuel specimen containing TRISO-coated fertile ThC_2 particles and TRISO-coated fissile UC_2 particles which was irradiated

in the Peach Bottom Reactor. The initial burn released 20% of the tritium and less than 1% of the ^{85}Kr . Most of the tritium and ^{85}Kr in the fertile particles was released during the grinding step, the remainder in the burning and leaching step. Grinding the fissile particle released most of the ^{85}Kr ; the subsequent burning and leaching steps released the tritium and remaining ^{85}Kr . About 3.5% of the gross gamma activity present in the fuel stick was carried over by the off-gas streams during the burning tests. Although the primary sintered metal filters collected most of this activity, 1% of the amount carried-over passed through the filter.

Although much more work needs to be done, particularly with higher burnup fuels and other fuel particle combinations, some general conclusion can be drawn. Most (98%) of the tritium and ^{85}Kr present in spent HTGR fuel will be released during the grind-burn step in the head-end operations, although the amounts released during grinding or burning will depend on the fuel particle being processed. Further, small amounts of fission products do pass the primary sintered metal filter and may have to be removed by other means.

Determination of the Radioactive Nuclides Present in the Off-Gas Stream
Generated by the Head-End Steps in Reprocessing HTGR Type Fuels

INTRODUCTION

A knowledge of the potential release of contamination to the environment is an essential part of the siting and hazard evaluation for any plant handling radioactive material. Studies are being performed at the Oak Ridge National Laboratory to determine the behavior of radioactive nuclides during the reprocessing of spent HTGR fuel. This paper is primarily concerned with the contaminants in the off-gas streams generated by the head-end reprocessing steps.

The fuel cycle for the HTGRs, such as are currently being sold by Gulf Energy and Environmental Systems, begins with a fuel containing thorium and ^{235}U . The thorium is converted to ^{233}U and when fuel equilibrium is reached, about half of the fissile material required for refueling is provided by the ^{233}U . Reprocessing the spent fuel will recover this ^{233}U together with some of the remaining ^{235}U . The fuel is in the form of microspherical particles, bonded into fuel sticks, and inserted into large hexagonal graphite blocks approximately 31.2 in. long and 14.2 in. across the flats as shown in Fig. 1. The fuel particles consist of kernels of thorium or uranium in either the oxide or carbide form with either a BISO or a TRISO protective coating. A BISO coating consists of an inner porous carbon buffer layer enveloped by an outer isotopic pyrocarbon layer. A TRISO coating consists of the inner porous carbon buffer layer and two isotopic pyrocarbon layers separated by a thin SiC layer. Fuel elements may contain all BISO-coated fuel particles, all TRISO-coated particles, or mixtures of both types of particles. Thus, in the Ft. St. Vrain reactor both the fertile (thorium dicarbide) particles and the fissile (uranium dicarbide) particles are TRISO-

F-1

HTGR FUEL

TRISO-II COATED PARTICLE

HEX BLOCK FUEL ELEMENT

coated, whereas only the fissile particles will be TRISO-coated in the large 1100 MW power reactors.

The head-end steps in the HTGR fuel reprocessing flowsheet first separates the fuel particles from the block graphite, then separate fertile from fissile particles and finally, puts the thorium and uranium into an aqueous solution. This solution is then sent to the solvent extraction step where the uranium-thorium separation and decontamination is effected. In the reference flowsheet, the fuel element is first crushed, and the crushed material burned to eliminate as much graphite as possible. During this step, BISO coatings are burned away, and the uranium/thorium kernel is exposed. Because of the high resistance of SiC to chemical attack, only the outer graphite coating of the TRISO particles burn away. The "burned TRISO" particles must be crushed to break the SiC coating, and then burned a second time to eliminate the inner graphite layers; thus exposing the uranium/thorium kernel. The exposed kernels are then leached with acid-thorex reagents (13 M HNO_3 , 0.05 M F^- , 0.1 M Al^{+++}) to dissolve the uranium and thorium. The particular series of head-end steps used depends on the TRISO-BISO particle combination present in the fuel element to be processed.

EXPERIMENTAL EQUIPMENT

The studies are carried out in a hot cell using irradiated fuel specimens weighing 10-25 grams. The burning steps are carried out in a stainless steel (Type 304) miniburner-filter assembly (Fig. 2). The burner body is placed in a vertical furnace which both furnishes the heat and supports the assembly. The filter holder, which has an independent heating system, will accommodate two sintered metal filters. Burner temperatures are controlled by varying either the oxygen content or the flow rate of the inlet gas stream. In-line infra-red analyzers monitor the off-gas CO and CO₂ content and a 200 channel analyzer

F-2

MINIBURNER-FILTER
ASSEMBLY

monitors the ^{85}Kr . Standard sieves are used for fuel particle separations. A Waring blender with the bowl modified by installing a purge gas inlet and outlet, is used to grind the TRISO particles to break the SiC layer.

EXPERIMENTAL RESULTS

The hot cell studies can be divided into two groups of experiments based on the source of the irradiated fuel specimens. The earlier group utilized fuel compacts obtained through the courtesy of the United Kingdom Dragon Reactor project. The current and continuing tests utilize fuel specimens obtained from a series of Recycle Test Elements (RTE) being irradiated in the Peach Bottom Reactor. Most of the candidate fuel particle combinations are included in these test elements.

The tests made with the Dragon compacts were designed primarily to obtain information on the behavior of the fuel particles in the head-end step, so only the ^{85}Kr and, in some tests, the tritium content of the off-gas generated by each head-end step were determined. We have completed the experimental work on Dragon compact 413-7-22, which contained BISO-coated sol-gel oxide particles prepared at ORNL, and on compact 19M, which contains a combination of large TRISO-coated thorium carbide (fertile) particles and smaller TRISO-coated uranium carbide (fissile) particles. The 413-7-22 compact was crushed, then separated into two samples which were burned in replicate experiments and the burner residues leached. The bulk of the ^{85}Kr (96.96% and 97.97%) and of the tritium (98.27% and 99.20%) was released during the burning step; the remainder reported to the off-gas generated during the leaching step.

A different experimental procedure was used for the 19M compact. First, the compact was crushed; then it was divided into two samples which were burned in replicate experiments. The burner ash from each experiment was sieved into a

fertile particle fraction (+20 mesh), a fissile particle fraction (-20, +42 mesh) and fine fraction (-42 mesh) containing the Al_2O_3 bed material plus broken particles. Each fertile and fissile fraction was ground, burned, and the residue leached. The fines residue was leached. Only the ^{85}Kr release data are available (Table 1).

Table 1. ^{85}Kr Release During the Processing of an Irradiated 19-M Dragon Compact with TRISO - TRISO Fuel Particles

Operation	^{85}Kr Release (% of total)
Initial Burning	7.35
Residue leach (-42 mesh)	0.57
Fertile fraction (+20 mesh)	
Grinding	3.77
Burning	3.63
Leaching	0.06
Fissile fraction (+42 mesh)	
Grinding	75.48
Burning	9.02
Leaching	0.10

In this test, 7.35% of the total ^{85}Kr found was released during the initial burning; 0.57% during the leaching of the fines fraction. Most of the ^{85}Kr in the fertile fraction was released in about equal amounts in the grinding step, 3.77% and the burning step, 3.63%. Grinding the fissile fraction released 75.48% of the ^{85}Kr with most of the remainder, 9.02%, reporting to the burner off-gas.

Experiments with the Recycle Test Element fuel specimens were more comprehensive than those with the Dragon compacts and were designed to permit sampling

the burner off-gases for both volatile and entrained fission products. Figure 3 F-3 shows a schematic flow diagram of the off-gas sampling train. The off-gas from the burner first passes through two sintered 20 μ porosity sintered Ni filters, held at 500°C (900°F); then, after cooling, into the Fiber Filter holder containing four grades of fibrous filter media. The filtered gas stream passes into a refluxing 6 M HCl scrubber, then into a cold (cell temperature) 4 M NaOH scrubber. The gas leaving the NaOH scrubber is dried, filtered to remove desiccant dust, and passed through the in-line ⁸⁵Kr, CO and CO₂ monitors. It is finally caught in the gas collection bag.

Fig-3

ORNL DWG 72-5306

OFF GAS TRAIN USED FOR RTE-7 HOT CELL TEST

Experimental work has been completed on the first irradiated fuel specimen from RTE-7. The fuel stick (0.5-in.-diam x 2 in. long) contained TRISO-coated ThC_2 fertile particles and TRISO-coated UC_2 fissile particles and had been in the Peach Bottom Reactor for 252 effective power days. It had cooled for 236 days before the experiment started. The fuel stick was placed in the mini-burner on an Al_2O_3 bed and burned (initial burn) to remove the binder carbon and outer pyrolytic carbon coatings. The burner residue was separated into three fractions; a fertile fraction consisting of all particles greater than 42 mesh, a fissile fraction containing all particles less than 42 mesh but greater than 80 mesh, and a fines fraction minus 80 mesh consisting of Al_2O_3 UO_2 bed material and broken particles. The fertile and fissile fractions were ground to break the SiC coating, burned, and the burner residue leached. The fines fraction was only leached.

The fission gas release for all grind, burn, and leach step is shown in Table 2. About 20% of the total tritium and less than 1% of the ^{85}Kr were released during the initial burning. Most of the tritium and about half of the ^{85}Kr associated with the fertile particle fraction was released during the grinding step; the remainder came off during the burning and leaching steps. Grinding ThC_2 fissile particle fraction released most of the ^{85}Kr and very little tritium. The burning step released most of the remaining ^{85}Kr and a little more tritium. Most of the remaining tritium and ^{85}Kr ^{was} were released during a 12 hr (750°C) "soaking" period. A small amount of tritium and ^{85}Kr (from broken beads) was released when the fine fraction was leached. In essence, 98+ percent of the tritium and ^{85}Kr were released during the grinding and burning steps and will be found in the combined carbon dioxide rich (90% percent) off-gas stream.

The distribution of the fission products along the off-gas train for the initial burn, the fertile particle fraction burn, and the fissile particle fraction burn is shown in Table 3. About 3.5% of the gross gamma activity present in

Table 2. Fission Gas Release for RTE-7 TRISO-TRISO Fuel

Operation	Percent of Total ^3H Released	Percent of Total ^{85}Kr Released
Initial burn	20.562	0.135
Fertile (+42 mesh) fraction		
Grind	33.771	1.263
Burn	2.685	0.989
Leach	0.008	0.106
Total	36.464	2.358
Fissile (+80 mesh) fraction		
Grind	1.431	70.072
Burn ^a	4.594	25.696
Soak ^b	35.803	1.565
Leach	0.042	0.091
Total	41.870	97.424
Fines (-80 mesh) fraction		
Leach	1.104	0.083

^a Three-hour active burning period.

^b Held for 12 hr at 750°C after completion of burning.

Table 3. Distribution of Fission Products in the Off-Gas Trains from RTE-7 Tests

Percent of total carry-over during	Gy (%)	⁹⁵ Zr (%)	⁹⁵ Nb (%)	¹⁰⁶ Ru (%)	¹³⁴ Cs (%)	¹³⁷ Cs (%)	¹⁴⁴ Ce (%)
Initial burn	7.91	0.052	0.019	0.534	19.82	14.34	0.081
Fertile fraction burn							
Metal filter-1	0.0261	0.006	0.007	0.107	0.029	0.019	0.008
Metal filter-2	0.0007	0.0001	0.0001	0.003	0.001	0.0006	0.0006
Fiber filters	---	---	---	0.010	0.0003	0.0002	0.0001
Acid scrub	0.720	---	---	---	0.519	0.989	0.010
Base scrub	0.100	0.004	0.0009	0.011	0.243	0.188	0.007
Subtotal	0.850	0.01	0.008	0.131	0.794	0.196	0.026
Fissile fraction burn							
Metal filter-1	85.11	82.81	88.40	75.20	73.09	77.90	82.79
Metal filter-2	5.96	17.03	11.32	23.98	6.07	6.24	16.98
Fiber filters	---	0.001	---	0.182	0.0005	0.0002	0.0006
Acid scrub	0.05	0.024	0.087	0.039	0.042	0.033	0.060
Base scrub	0.10	0.007	0.005	0.010	0.240	0.178	0.007
Subtotal	91.23	99.872	99.812	99.339	79.410	84.454	99.888

the fuel stick was carried over by the off-gas streams. Six isotopes, ^{95}Zr , ^{95}Nb , ^{106}Ru , ^{134}Cs , ^{137}Cs , and ^{144}Ce accounted for ~90% of this activity. Fission products were found on the metallic filter, on the fiber filters and in the scrubber solutions.

The off-gas from the initial burn was only filtered through one sintered Ni filter. The high percentage of ^{134}Cs (19.8%) and ^{137}Cs (14.3%) found on the filter apparently came from surface contamination rather than from broken fuel particles. The amount of activity found on off-gas trains after the fertile particle burn was less than 1% total activity carried over, in part due to the fact that the fertile particles only contribute about 10% to the total fission product content of the fuel stick. Most of the activity which was carried over during the fertile particle burn passed through the filters and was found in the scrubber solutions. The filters were much more effective during the fissile particle burn. Most of the activity carried over^{all} was found on the sintered metal filters. Nevertheless, small amounts of activity passed through the filters and were found in the scrubber solutions.

While much more work needs to be done, particularly with higher burn-up fuels, before the fission gas release and fission product carry-over patterns are fully characterized, some general conclusions can be drawn: Most of the ⁸⁵Kr (98%) present in HTGR fuels is easily released during the burning and grinding steps. While 98-99% of the tritium will be released during the burning and grinding steps, the tritium release rates during burning may be slower than those for ^{85}Kr , thus requiring longer processing time. Finally, small amounts of fission products do pass through the sintered metal filters and may have to be removed by other means.